Formation of Nonspherical Particles with Uneven Surface in Emulsion Copolymerization of Styrene and Methacrylic Acid with Nonionic Emulsifier[†]

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Summary: Emulsion copolymerization of styrene and methacrylic acid with nonionic emulsifier and potassium persulfate as initiator gave nonspherical copolymer particles having uneven surface. The formation was based on the coagulation of byproduct nano-sized (ca. 35 nm) particles, which were formed throughout the copolymerization until monomer phase disappeared, onto main submicron-sized (234 ∼ 445 nm) particles.

Keywords: emulsion polymerization; nonionic emulsifier; nonspherical particle; nucleation

Introduction

Carboxylated polymer emulsions have been widely used in various industrial fields.[1,2] In recent years, such particles are applied as carrier for bioactive protein to create bioreactors and biosensors,[3–5] and some researchers tried to use them as ion exchangers.[6,7] In both cases, only functional groups at particle surfaces are effective, so many fundamental studies have been conducted on the evaluation and control of the predominant distribution of carboxyl groups at particle surfaces.[8–15]

Recently, it was found that nonionic emulsifier was incorporated inside particles prepared by emulsion copolymerization of styrene (S) and methacrylic acid (MAA)[16–18] in a series of investigations on the preparation of multihollow particles by post treatments of carboxylated polymer particles with alkali.[19–21] Moreover, in the studies, we noticed that S-MAA copolymer, P(S-MAA), particles with uneven surface could be obtained by the emulsion copolymerization.

It is an important subject to study the formation of nonspherical polymer particles on both academic and industrial perspective.[22,23] We have been preparing some submicron-sized, nonspherical polymer particles having raspberry-like,[24] octopus ocellatus-like[25] and golf-ball-like shapes[26,27] by seeded emulsion polymerization, and clarified their formation mechanisms.

In this article, the formation mechanism of the nonspherical P(S-MAA) particles with uneven surface by the emulsion copolymerization described above will be clarified.

Experimental Part

Materials

S (Mitsubishi Chemical Co, Japan) and MAA (Nacalai Tesque Inc., Kyoto, Japan) were purified by distillation under reduced pressure. Potassium persulfate (KPS, (Nacalai Tesque Inc., Kyoto, Japan)) of analytical grade was purified by recrystallization. Commercial grade polyoxyethylene nonylphenyl ether nonionic emulsifier (Emulgen 911, Kao Corp, Tokyo, Japan), with formula $C_9H_{19}{-}C_6H_4{-}O(CH_2CH_2$

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O)$_{10.9}$OH (hydrophile-lipophile balance (HLB) = 13.7) and potassium hydroxide (KOH, Nacalai Tesque Inc., Kyoto, Japan) were used as supplied. The water used in all experiments was obtained from a Elix® UV (Millipore Co., Ltd.; Japan) purification system and had a resistivity of 18.2 $M\Omega\,cm^{-1}$.

Emulsifier-containing and Emulsifier-free Emulsion Copolymerizations

P(S–MAA) particles were prepared by batchwise emulsion copolymerization in a glass reactor equipped with an inlet of N_2, a reflux condenser, and a half-moon type stirrer under the conditions listed in Table 1. The stirrer was set at the interface between the monomer and aqueous phases and the stirring rate was 240 rpm.

During emulsion copolymerization, at regular intervals, the polymer emulsions containing 1~2 g polymer were pipetted out from the bottom of the reactor after monomer droplets floated up by stopping the stir. The samples were cooled rapidly after adding a few drops of hydroquinone aq. solution to stop the polymerization. The overall conversion was determined by gravimetric method. The S concentration in the particles was calculated by subtraction of the saturated S concentration in the water phase from the conversion measured by gas chromatography (GC) (Shimadzu Corporation, GC-18A). The particle morphology was observed with a transmission electron microscope (TEM) (JEM-1230, JEOL Ltd.; Tokyo, Japan).

Heat Treatment

Final emulsion of 10 mL was added into 100 mL methanol to remove quickly residual monomers from particles and then carried out the ultracentrifugal washing with deionized water three times to replace the methanol. The purified emulsion (solid content was about 10% and the pH was about 4.0) was placed in a stainless steel pressure-resistant vessel having a polytetrafluoroethylene (PTFE) 50 mL-capacity inner containers, and the vessel was dipped in an oil bath at 130 °C (higher than the Tg of the base polymer, 95 °C) for 24 h.

Number of the Particles in Polymer Emulsion

Number of particles in emulsion was calculated from the amount of polymer and number-average particle diameter measured by dynamic light scattering spectrograph (DLS, FPAR-1000RK, Otsuka Electronics Co. Ltd., Osaka, Japan).

Partitioning of Emulgen 911

In order to measure the partitioning of Emulgen 911 between water and monomer phases, monomer emulsion was prepared at the same recipe as that of the copolymerization excepting KPS. The monomer emulsion was stirring at 70 °C for 1 h and a part of monomer (about 5 mg) was withdrawn from the monomer layer after stopping the stirring. Quantitative analysis of Emulgen 911 was conducted by gel permeation chromatography (GPC, TOSOH Corporation) according to the previous work.[16]

Amount of Byproduct Small Particles

Byproduct small particles were obtained from supernatant after main large particles were sedimented by centrifugation. The

Table 1.
Recipes of emulsifier-containing and emulsifier-free emulsion copolymerizations[a].

Ingredients		Emulsifier-containing	Emulsifier-free
Styrene	(g)	55	55
Methacrylic acid	(g)	5	5
Potassium persulfate	(g)	0.24	0.24
Emulgen 911	(g)	4	–
Water	(g)	540	540

[a] 70 °C under N_2 with a stirring rate of 240 rpm.

dried byproduct small particles were dissolved into Tetrahydrofuran (THF) and the solution was analyzed by GPC. The amount of the small particles was determined from peak area due to polymer by using the calibration curve of corresponding polymer standard. At the same time, the average molecular weight of the byproduct small particles was measured.

Results and Discussion

Figure 1 shows TEM (a, b) and SEM (a', b') photographs of washed P(S-MAA) particles, which were prepared by batchwise emulsion copolymerization under the conditions listed in Table 1, before (a, a') and after (b, b') heat treatment at 130 °C for 24 h. The untreated particles had uneven surfaces, but the uneven surfaces were changed to smooth ones by the heat treatment. This indicates that the uneven surfaces of the untreated P(S-MAA) particles are formed under thermodynamically unstable state.

Figure 2 shows SEM photographs of unwashed P(S-MAA) particles at different conversions. At 5 and 9% conversions, both particles were smaller than 200 nm and the surfaces were unclear. When the conversion increased up to 58%, particles had obviously uneven surface, which might be formed by coagulation of byproduct small particles onto the preformed main particles. At 92% conversion, particles still had uneven surface although the roughness was lower than that of the particles at 58% conversion.

Figure 3 shows SEM photographs of P(S-MAA) particles at different conversions after removing the byproduct small particles by centrifugal washing. The particles had nonspherical shape with uneven

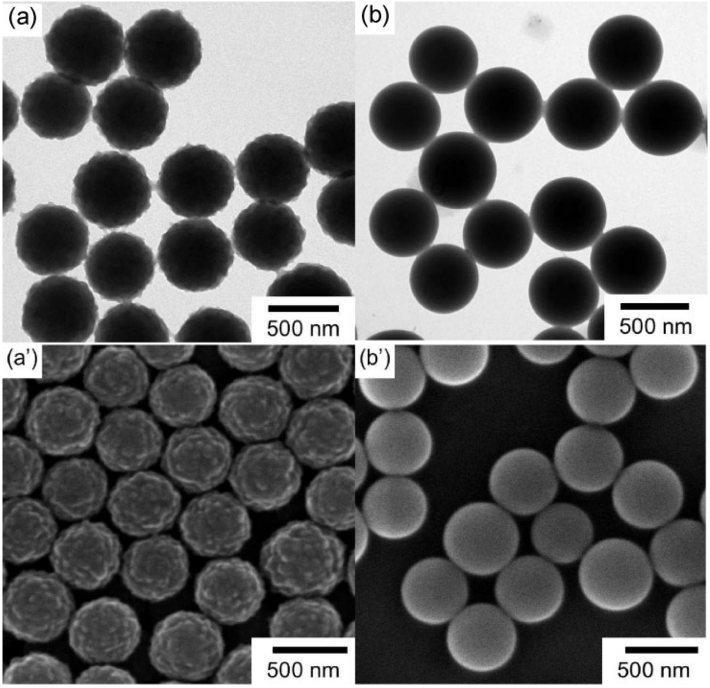

Figure 1.
TEM (a, b) and SEM (a', b') photographs of P(S-MAA) particles prepared by emulsion copolymerization with nonionic emulsifier (Emulgen 911) under the conditions listed in Table 1 after 3 times centrifugal washing, before (a, a') and after (b, b') heat treatment at 130 °C for 24 h.

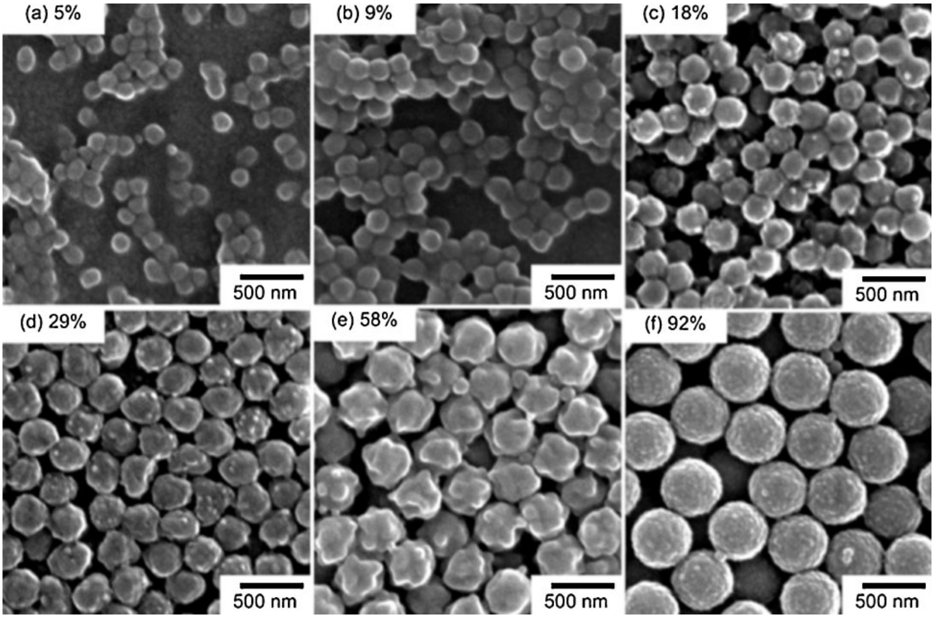

Figure 2.
SEM photographs of unwashed P(S-MAA) particles at different conversions prepared by emulsion polymerization under the conditions listed at Table 1.

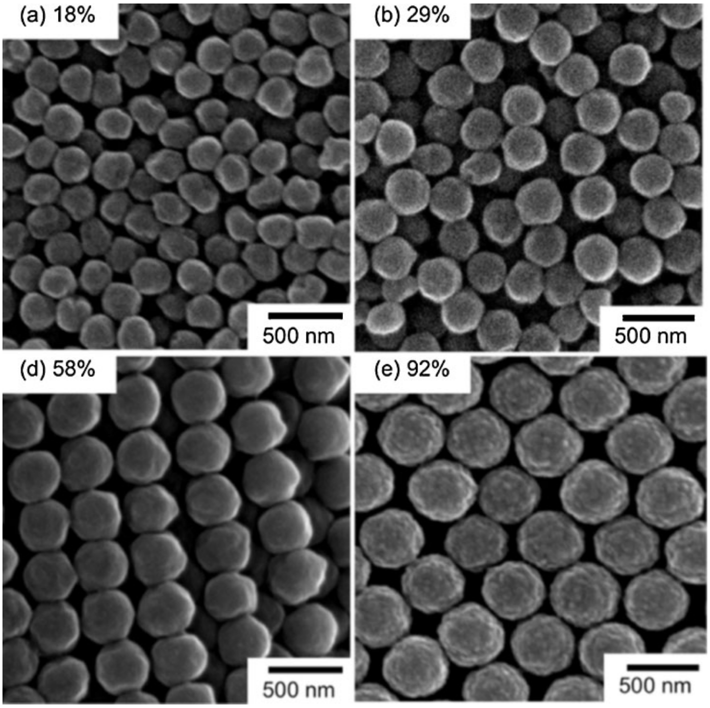

Figure 3.
SEM photographs of P(S-MAA) particles at different conversions, after three times ultracentrifugal washing, prepared by emulsion polymerization under the conditions listed at Table 1.

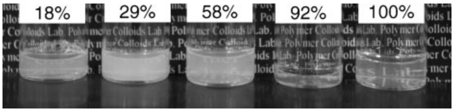

Figure 4.
Photographs of supernatants obtained from P(S-MAA) emulsions at different conversions after removal of large main particles by centrifugal washing.

surface, although the surface roughness after washing was somewhat lower than that before washing. These observations (Figures 2 and 3) indicate that the non-spherical particles should be formed by coagulation of the byproduct small particles onto the large main particle during the copolymerization, rather than during the drying.

Figure 4 shows photographs of supernatants obtained from the emulsions at the different conversions after centrifugal separation of the main particles at 14,000 rpm for 15 min. Below 58% conversions, the supernatants were turbid, while those of samples above 92% conversion were almost transparent.

Figure 5 shows size distributions of particles in the supernatants (byproduct small particles) and precipitates (main large particles). The results indicate that there always were byproduct small particles in the emulsions during the copolymerization. The sizes of byproduct particles at 58% or lower conversion were almost the same (32∼36 nm), regardless of the conversion, and then it increased to about 90 nm until 92% conversion. On the other hand, main large particles increased from 235 nm to 444 nm with the conversion (18%∼100%). This suggests that at least less than 58% conversion, the small particles were always formed and captured by the main particles within a certain time.

The amounts of the byproduct small particles and the main large particles in emulsions at the different conversions are shown in Table 2. The number of the main large particles was kept at the constant ($\approx 2 \times 10^{12}$ /mL), which is smaller than that ($10^{13} \sim 10^{15}$ /mL) prepared by a general emulsion polymerization. On the other hand, the number of the byproduct small particles decreased dramatically at the final stage of the polymerization. Even though the weight percentages of the byproduct small particles were less than one percent, their numbers were 10∼20-fold to that of the main particles below 58% conversion. *M*n values of these polymers forming the byproduct small particles were only 30×10^3 below 58% conversion, where the sizes were kept at about 35 nm. Above that, where the sizes increased to about 87 nm, the *M*n value increased to 112×10^3, which was still smaller than that of the main particles. These indicate that the polymers forming the byproduct small particles were prepared not in preformed particles, but in the aqueous medium below 58% conversion based on the homogeneous nucleation.

Piirma[28] and Ozdeger[29] reported that the partitioning of nonionic emulsifier between monomer and aqueous phases played a major role in determining the nucleation mechanism in emulsion polymerizations. Therefore, the amount of Emulgen 911 located at monomer and aqueous phases was measured. Almost all the emulsifier (about 95% of total emulsifier) partitioned to the monomer phase at the starting of the copolymerization.

That is, the concentration of the emulsifier in the aqueous medium at starting of the copolymerization was lower than its critical micelle concentration (0.72 mmol/L) in aqueous solution saturated with styrene and MAA. This suggests that the particle nucleation in the early stage of the copolymerization is based on not micellar nucleation but homogeneous nucleation as well as emulsifier-free emulsion copolymerization. This is supported by the data on conversion-time curves of Emulgen 911-containing and emulsifier-free emulsion copolymerizations (see Figure 6), in which both copolymerization rates were almost the same in 2 h (conversion <20%). In both cases, monomer droplets (layer) disappeared around 60% conversion.

Figure 7 shows SEM photographs of unwashed P(S-MAA) particles prepared by

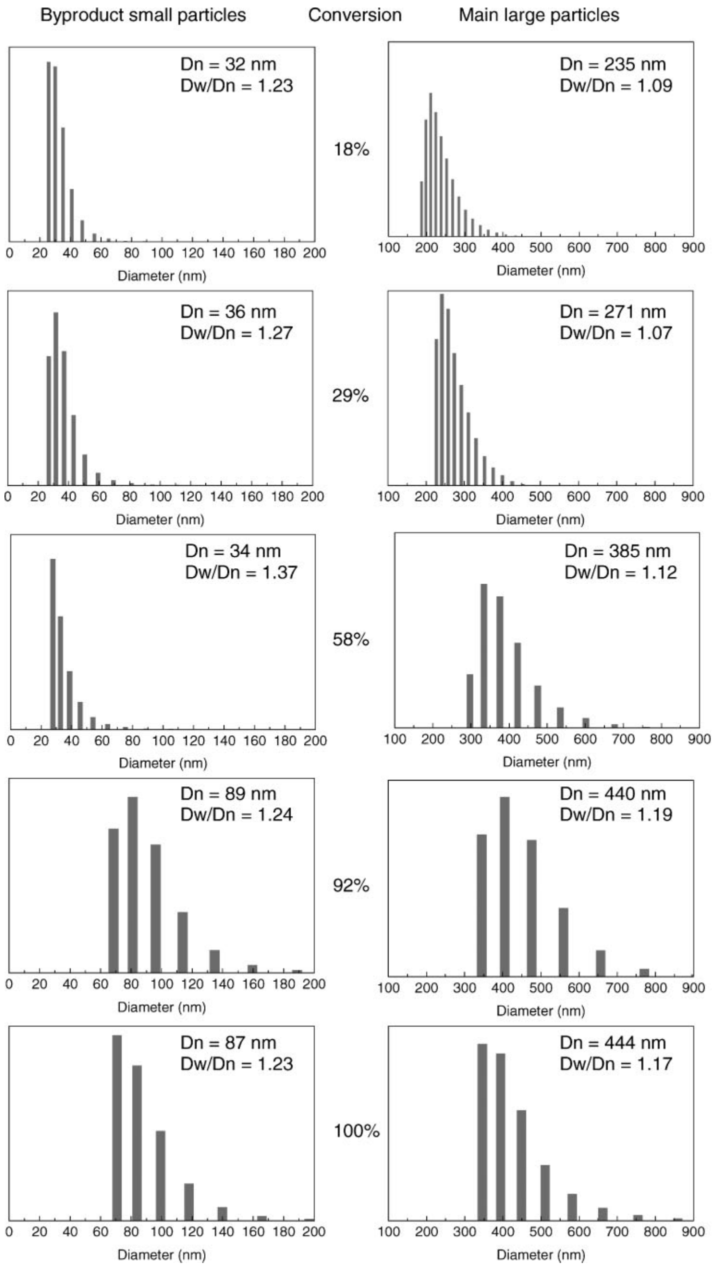

Figure 5.

Size distributions of particles in supernatants (byproduct small particles) and precipitates (main large particles) of emulsions at different conversions.

the emulsifier-free emulsion copolymerization at 7 and 97% conversions. The particles were monodispersed and had spherical shape with smooth surface, and no byproduct small particle was observed. In addition, the final particles were smaller than the main large particles prepared by the Emulgen 911-containing emulsion

Table 2.
Particles in emulsion at different conversions.

Conversion	(%)	18	58	92	100
Byproduct small particles					
Amount	(wt%)	0.72	0.78	0.02	0.14
Number	($\times 10^{12}$/mL)	29.8	36.2	0.04	0.4
Mn		27,000	21,200	115,800	111,900
Mw		64,200	45,200	257,900	435,800
Main large particles					
Number	($\times 10^{12}$/mL)	2.34	1.86	1.99	2.09
Mn		–	–	–	207,600
Mw		–	–	–	466,000

[a]Based on the weight of total polymer particles.

copolymerization. In other words, the number of particles (1.58×10^{13}/mL) in the emulsifier-free system was higher than that of the main large particles in Emulgen 911-containing system.

From the above results, we could deduce the formation mechanism of the nonspherical particles with uneven surface as follows. Partition of almost all the nonionic emulsifier into the monomer phase, which gives lower emulsifier concentration in the aqueous medium than critical micelle concentration, leads to the homogeneous nucleation. During the total interfacial area of the primary particles is not enough large to capture all of oligomer radicals formed in the aqueous medium, some oligomers aggregate in the aqueous medium, resulting in small byproduct particles continuously. Because main (preformed) and byproduct particles do not have efficient stability due to low amount of adsorbed emulsifier, most of byproduct small particles coagulate onto the large main particle, and result in nonspherical particles with uneven surface. Until the disappearance of the monomer phase, monomer was preferentially supplied from the monomer phase to polymerizing particles over emulsifier, so that the emulsifier concentration in the monomer phase was increased.[30] When the monomer phase disappeared at 60% conversion, rather amount of emulsifier remained in the monomer phase instantly transfers into the aqueous medium and are adsorbed on the particles, which depresses the coagulation of the byproduct particles onto the main particles. Therefore, above 60% conversion, the coagulation and enlargement of the byproduct small particles gradually proceeded at the same time. At the completion of the copolymerization, the uneven surface of the main particles remains uneven because of high viscosity with in the particles.

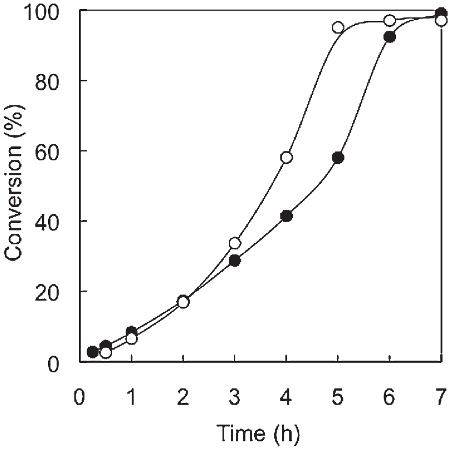

Figure 6.
Conversion-time curves of emulsion copolymerizations of styrene and MAA without (open circle) and with (closed circle) Emulgen 911.

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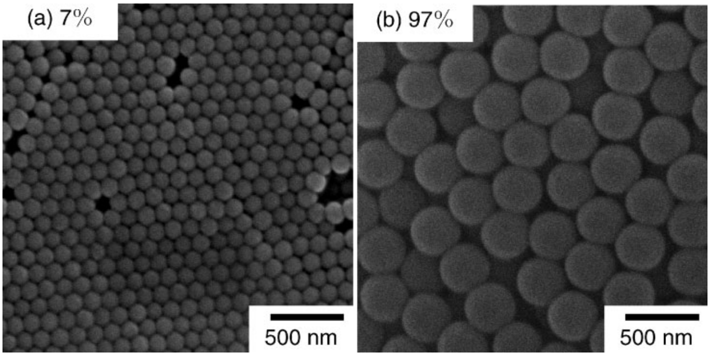

Figure 7.
SEM photographs of unwashed P(S-MAA) particles prepared by emulsifier-free emulsion copolymerization at different conversions.

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